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INTRODUCTION

In a recent article, Sharma[1] has shown that the contribution of polarizability anisotropy to Rayleigh scattering given in literature by molecules is valid only for diatoms and only in the high temperature (high rotational quantum number) limit. It was also shown that this error is introduced by approximating the constraint imposed by the conservation of angular momentum to be $1/4$, the high temperature value of the vector coupling coefficients. The introduced error has the opposite sign for N_2 and O_2, two important molecules. The magnitude of the calculated error monotonically decreased as the temperature is increased; for N_2 it decreased from 4% to 2% while for O_2 it decreased from -11% to -5% as the temperature increased from 100 to 300 K. Since the measurement of depolarization ratio[2,3] is used to arrive at the ratio of anisotropic polarizability to isotropic (average) polarizability, it was considered advisable to calculate this error for molecules. In this article we have calculated the depolarization ratio of the Rayleigh scattered radiation for three molecules, a simple $^1\Sigma$ diatom (N_2), a symmetric top (CH_3Cl), and an asymmetric top (H_2O), and compared the calculated values with the measured ones. We show that the neglect of constraints imposed by the conservation of angular momentum overestimates the ratio of anisotropic polarizability to isotropic (average) polarizability by a factor of about 2 for N_2, about 1.7 for CH_3Cl, and about 2.2 for H_2O.

FORMULATION

The differential cross section for Rayleigh scattering through angle β by a $^1\Sigma$ diatomic molecule (N_2) is given by the expression[1]

$$\frac{d\sigma}{d\Omega}(\beta) = \frac{\omega\omega_s^3}{c^4}\sum_\alpha I_1(\alpha,j_i,j_f) \times I_2(\alpha), \quad (1)$$

with

$$I_1(\alpha,j_i,j_f) = \frac{\chi_{\alpha,0}^2}{(2\alpha+1)}C^2(j_i\alpha j_f;0,0), \quad (2)$$

and

$$I_2(\alpha) = \sum_q \left| \sum_{M,p} \varepsilon_p\left(\frac{\pi}{2},\varphi_s\right)\varepsilon_M\left(\frac{\pi}{2},\phi_i\right)d_{p,q-M}^1(\beta) \right.$$
$$\left. \times C(11\alpha;M,q-M) \right|^2, \quad (3)$$

where ω is the frequency (s^{-1}) of the incident radiation, ω_s is the frequency (s^{-1}) of the scattered radiation, and α is the rank of the polarizability tensor,[4]

$$\chi_{00} = C(110;00)\alpha_{zz} - C(110;1,-1)(\alpha_{xx}+\alpha_{yy})$$
$$\equiv -\left(\frac{1}{3}\right)^{1/2}(\alpha_{zz}+\alpha_{xx}+\alpha_{yy}) = -(3)^{1/2}\alpha_{av}, \quad (4)$$

with α_{av} being the average polarizability,

$$\chi_{2,0} = C(112;00)\alpha_{zz} - C(112;1,-1)(\alpha_{yy}+\alpha_{xx})$$
$$= \left(\frac{2}{3}\right)^{1/2}\left(\alpha_{zz} - \frac{1}{2}(\alpha_{yy}+\alpha_{xx})\right) \equiv \left(\frac{2}{3}\right)^{1/2}\gamma, \quad (5)$$

with γ being the polarizability anisotropy of the $^1\Sigma$ diatomic molecule, and

$$\chi_{2,\pm 2} = \left(\frac{3}{8}\right)^{1/2} C(112;\pm 1,\pm 1)(\alpha_{xx}-\alpha_{yy}\pm 2i\alpha_{xy})$$
$$= \left(\frac{3}{8}\right)^{1/2}(\alpha_{xx}-\alpha_{yy}\pm 2i\alpha_{xy}). \quad (6)$$

The change in magnetic quantum number (projection of the angular momentum of the molecule on the space-fixed axis) of the molecule in Eq. (3) is represented by q. C in Eqs. (2)–(6) is the Clebsch-Gordan (vector coupling) coefficient; $C^2(j_i\alpha j_f;0,0)$ ensures the conservation of angular momentum. The conservation of angular momentum also requires that the differences in the projections of the electric vectors of the incident and scattered photons on a space-fixed z axis
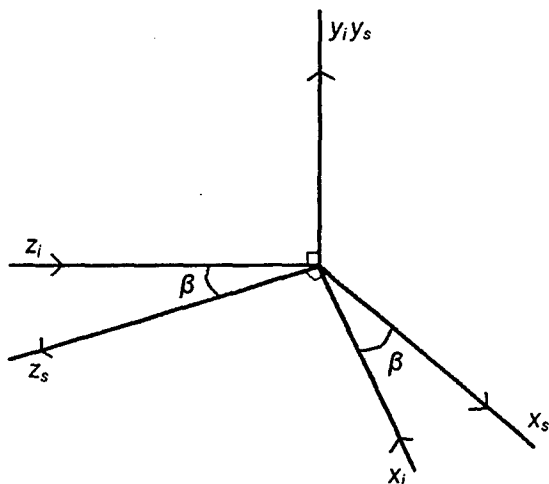
FIG. 1. The two coordinate systems embedded in the incident and scattered beams.
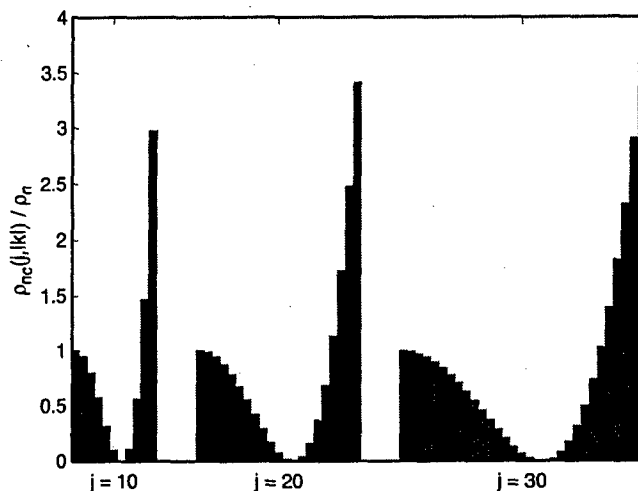

FIG. 2. The ratio of the calculated depolarization ratio to that given in literature, ρ_{nc}/ρ_n, for CH_3Cl as a function of j and $|k|$ with $|k|$ increasing from right to left.

equal q; this is ensured by the Clebsch-Gordan coefficient $C(11\alpha;M,q-M)$, M being the projection of the electric vector of the incident photon and $q-M$ being the projection of the electric vector of the scattered photon on the space-fixed z axis. The plane containing the incident and scattered photons, the scattering plane, is the xz plane of the space-fixed coordinate system. The incident and the scattered photons travel along the z axis of the coordinate systems fixed in the incident and scattered beams; these two coordinate systems share a common y axis perpendicular to the scattering plane (Fig. 1). The space-fixed coordinate system is taken to be the one fixed in the incident beam. The ε_M and ε_p are projections of the electric vectors of the incident and scattered photons on the spherical coordinate systems embedded in the respective beams and $d^1_{p,q-M}(\beta)$ is the rotation matrix of order 1 that transforms the projection p to $q-M$, its projection on the space-fixed coordinate system (incident beam), via rotation by the scattering angle β around the y axis common to the two beams.

When extending Eq. (1) to polyatomic molecules two complications arise.

(1) A $^1\Sigma$ *diatomic molecule rotates with its plane of rotation perpendicular to its angular momentum vector.* The projection of the angular momentum vector on the internuclear axis k, a good quantum number, is zero. The wave function of the molecule in the rotational level j is given by $|j,k=0,m\rangle=[2j+1/8\pi^2]^{1/2}D^{j*}_{m,0}(\Omega)$, where m is the magnetic quantum number (projection of the angular momentum vector on the space-fixed axis) and D is the rotation matrix[5] of order j. A $^1\Sigma$ polyatomic molecule with an n-fold axis of symmetry ($n\geqslant3$) has two equal moments of inertia (symmetric rotor), e.g., CH_3Cl, and rotates with its plane of rotation at a fixed angle to its angular momentum vector. The projection of the angular momentum vector on the axis of symmetry of the molecule k, still a good quantum number, varies like m from $-j$ to $+j$ in steps of 1. Except for $k=0$ the rotational levels for a given value of k are doubly degenerate, the ones with $+k$ and $-k$ having the same energy. The wave function of the molecule in the rotational level j is given by[5] $|j,k,m\rangle=[2j+1/8\pi^2]^{1/2}D^{j*}_{m,k}(\Omega)$. The symmetry arguments

show that $\chi_{2,0}$ is the only nonzero polarizability anisotropy. Equation (2) now becomes

$$I_1(\alpha;j_i,k_i;j_f,k_f)=\frac{\chi^2_{2,0}}{(2\alpha+1)}C^2(j_i\alpha j_f;k_i,0,k_f)\delta_{k_f,k_i}. \quad (7)$$

For Rayleigh scattering ($j_i=j_f$ and $k_i=k_f$) the vector coupling coefficient in Eq. (7) becomes

$$C^2(j2j;k,0,k)=\frac{(3k^2-j(j+1))^2}{[j(j+1)(2j-1)(2j+3)]}. \quad (8)$$

The Rayleigh scattering due to polarizability anisotropy now depends not only on the rotational quantum number j but also very strongly on its projection on the molecular axis of symmetry k (Fig. 2). For $k=0$ this value approaches its classical limit of $1/4$ for large j, but for $k\approx j(j+1)/\sqrt{3}$ it is near zero, and for $k=j$ the large j limit is 1, four times the value given in literature.

A polyatomic molecule with three unequal moments of inertia (asymmetric rotor), e.g., H_2O, does not rotate with its plane of rotation at a fixed angle to its angular momentum vector. The projection of the angular momentum vector on the axis of symmetry of the molecule k is no longer a good quantum number. The rotational wave function of the molecule in the rotational level j is now given by a linear combination of those of a symmetric rotor with a suitably chosen axis of symmetry for the molecule (for H_2O along the dipole moment),

$$|j_\tau,m,\pm\rangle=\sum_{k'}^{j}a_{k'}|j,k',m,\pm\rangle, \quad (9)$$

where k' takes even or odd non-negative integral values up to j and $\pm$ refers to the parity of the suitably normalized symmetric rotor wave functions upon changing k' to $-k'$, τ being the index that has $(2j+1)$ values from $-j$ to j and orders the wave functions according to energy—the larger the energy, the higher the value of τ. We constructed the rotational wave functions at the rigid rotor level of approximation following Zare[5] and Dennison and Hecht.[6]

TABLE I. Six sets of values of the three polarizabilities (in $\mathring{A}^3$) taken from the literature and α_{av}, β^2, $\chi_{2,0}$, and $\chi_{2\pm2}$ derived from them. The data sets with references are A (Ref. 8), B (Ref. 9), C (Ref. 10), D (Ref. 11), E (Ref. 12), and F (Ref. 3).

Data set	α_{xx}	α_{yy}	α_{zz}	α_{av}	β^2	$\chi_{2,0}$	$\chi_{2,2}$
A	1.503	1.431	1.451	1.4617	0.004 144	−0.130 64	0.044 09
B	1.651	1.226	1.452	1.443	0.135 651	0.011 023	0.260 26
C	1.696	1.221	1.519	1.4787	0.172 879	0.049 398	0.290 88
D	1.850	1.350	1.480	1.560	0.201 900	−0.097 98	0.306 19
E	1.765	1.360	1.590	1.5417	0.123 775	0.022 454	0.248 01
F	1.5284	1.4146	1.4679	1.4703	0.009 726	−0.002 939	0.069 69

(2) *The polarization anisotropy for asymmetric tops is no longer given by Eq. (3) but by the magnitude of anisotropy.*[7]

$$\beta^2 = \tfrac{1}{2}[(\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{zz} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2 + 6((\alpha_{zx})^2 + (\alpha_{yz})^2 + (\alpha_{xy})^2)]. \tag{10}$$

This expression reduces to Eq. (3) when $\alpha_{xy} = \alpha_{yz} = \alpha_{zx} = 0$ and $\alpha_{xx} = \alpha_{yy}$; for H_2O only the former holds and

$$\beta^2 = \tfrac{1}{2}[(\alpha_{zz} - \alpha_{xx})^2 + (\alpha_{zz} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2]$$
$$= \gamma^2 + (\chi_{2,2})^2 + (\chi_{2,-2})^2, \tag{11}$$

with $\gamma = (\alpha_{zz} - (1/2)(\alpha_{yy} + \alpha_{xx}))$ and $\chi_{2,+2} = \chi_{2,-2} = (3/8)^{1/2}(\alpha_{xx} - \alpha_{yy})$.

It is at once seen that when the magnitude of anisotropy is used to derive the depolarization ratio, any constraints imposed by the conservation of angular momentum are absent. Table I gives six sets of values of the three polarizabilities in $\mathring{A}^3$ taken from the literature and α_{av}, β^2, $\chi_{2,0}$, and $\chi_{2\pm2}$ derived from them. The polarizabilities given here take the z axis along the symmetry axis of the molecule (axis with intermediate moment of inertia) and the y axis perpendicular to the plane of the molecule (axis with the greatest moment of inertia).

If the incident beam travels along the z axis (polarization vector along the x axis or y axis) and the scattered radiation is observed along the x axis (polarization vector along the z axis or y axis), as shown in Fig. 1, the depolarization ratio ρ is defined as the ratio of the intensity of light with polarization vector rotated by 90° (polarization vector along the y axis or z axis), $I_\perp$, to the intensity of light with unchanged polarization vector (polarization vector along the z axis or y axis), $I_\parallel$. Sharma[1] has shown that for unpolarized (natural) light the contribution of $I_2(\alpha=2)$, Eq. (3), to $I_\perp$ is unity while its contribution to $I_\parallel$ is 7/6. For unpolarized (natural) light the calculated depolarization ratio ρ_{nc} for N_2 is then given by

$$\rho_{nc}(j) = \frac{I_\perp}{I_\parallel} = \frac{6\gamma^2 C^2(j2j;00)}{45(\alpha_{av})^2 + 7\gamma^2 C^2(j2j;00)}. \tag{12a}$$

For the polarized light the contribution of $I_2(\alpha=2)$, Eq. (3), to $I_\perp$ is 1/2 while its contribution to $I_\parallel$ is 2/3. The depolarization ratio then becomes

$$\rho_{0c}(j) = \frac{I_\perp}{I_\parallel} = \frac{3\gamma^2 C^2(j2j;00)}{45(\alpha_{av})^2 + 4\gamma^2 C^2(j2j;00)}. \tag{12b}$$

The value of ρ_n given in literature is[13]

$$\rho_n = \frac{I_\perp}{I_\parallel} = \frac{6\gamma^2}{180(\alpha_{av})^2 + 7\gamma^2}, \tag{12c}$$

which approximates $C^2(j2j;00) = j(j+1)/(2j-1)(2j+3)$ by 1/4, independent of j, and hence of temperature, as well as of the molecular species involved. The earlier literature[2,3,7] has completely ignored these constraints[1] and has given ρ_n and ρ_0 by Eqs. (12a) and (12b) omitting $C^2(j2j;00)$ and overestimating the depolarization ratio by about a factor of 4 for $^1\Sigma$ diatoms. Alternatively from a measured value of the depolarization ratio the derived γ/α_{av} is an overestimate by a factor of about 2 for $^1\Sigma$ diatoms. As pointed out earlier[1] there is negligible error involved in approximating the vector coupling coefficient $C^2(j2j;00)$ by 1/4 for N_2 at 300 K. Taking $\gamma = 0.691\ \mathring{A}^3$ from Asawaroengchai and Rosenblatt[14] and $\alpha_{av} = 1.738\ \mathring{A}^3$ from Zeiss and Meath[15] we obtain $\rho_{0c} = 2.6 \times 10^{-3}$, 1/4 times the measured value of $(0.96 \pm 0.14) \times 10^{-2}$ by Murphy[3] at room temperature. The depolarization ratio for a symmetric top, a function of j and $|k|$, is given by

$$\rho_{nc}(j,|k|) = \frac{I_\perp}{I_\parallel}, \tag{13}$$

with

$$I_\perp = \frac{2\gamma^2}{15} \frac{(3k^2 - j(j+1))^2}{[j(j+1)(2j-1)(2j+3)]} \tag{13a}$$

and

$$I_\parallel = (\alpha_{av})^2 + \frac{7}{6} \frac{2\gamma^2}{15} \frac{(3k^2 - j(j+1))^2}{[j(j+1)(2j-1)(2j+3)]}. \tag{13b}$$

Assuming that the energy of interaction of the nuclear spins with the rotational motion is much smaller than the width of the laser beam used to measure the depolarization ratio (Appendix), Fig. 3 gives a plot of ρ_{nc}/ρ_n for CH_3Cl as a function of temperature. Even though the value of ρ_{nc}/ρ_n is a strong function of k it shows little variation as a function of temperature, remaining about 0.72 over the 100–300 K temperature range. Taking the values of α_{av} and γ from Bridge and Buckingham[2] and those of rotational constants from Herzberg[7] we get $\rho_{0c} = 1.4 \times 10^{-3}$. The measured value of the depolarization ratio by Bridge and Buckingham[2] at room temperature is 7.66×10^{-3}. This value is close to the value $\rho_{0c}(4/0.72) = 7.78 \times 10^{-3}$ one would get by ignoring the constraints imposed by the conservation of angular momentum.

The differential cross section for Rayleigh scattering by an asymmetric rotor is given by Eq. (1) with
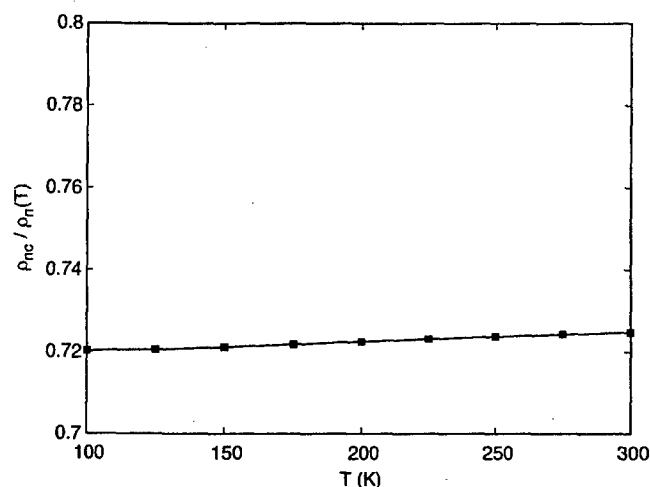
FIG. 3. The ratio of the calculated depolarization ratio to that given in literature, ρ_{nc}/ρ_n, for CH_3Cl as a function of temperature.

FIG. 5. The ratio of the calculated depolarization ratio to that given in literature, ρ_{nc}/ρ_n, for water vapor as a function of temperature for the six sets of polarizability values given in Table 1.

$$I_1(j_\tau, \alpha) \equiv \frac{1}{(2\alpha+1)} \left| \sum_{k_i, k_f, \kappa} \chi_{\alpha,\kappa} a_{k_i} a_{k_f}^* C(j_\tau \alpha j_\tau; k_i, \right.$$

$$\left. - \kappa, k_f) \delta_{k_f k_i - \kappa} \right|^2. \tag{14}$$

To calculate $I_1(j_\tau, \alpha=2)$ we have computed the rotational wave functions for the ground vibrational state of H_2O at the rigid rotor level of approximation. We now calculate ρ_{nc} assuming that (Appendix) the energy of interaction of the nuclear spins with the rotational motion is much smaller than the width of the laser beam used the measure the depolarization ratio (~1 MHz). A plot of ρ_{nc}/ρ_n as a function of j_τ (with τ increasing from left to right for each j) for $j=1-9$ is shown in Fig. 4; the value for $j=0$ being identically equal to zero is not shown. Although this ratio approaches 3–4, depending on the values of the polarizabilities used, for the lowest and highest values of τ as j approaches nine, it remains close to zero independent of j for middle values of τ, just as it approaches zero for the value of $|k|$ halfway between 0 and j for symmetric tops. Figure 5 gives a plot of

ρ_{nc}/ρ_n as a function of temperature for the six sets of the polarizability data. The six data sets divide into two groups; the ratio of ρ_{nc}/ρ_n for the first group (data sets B, C, E, and F) decreases from about 1.32 to about 1.27 while for the second group (data sets A and D) it decreases from about 1.24 to about 1.18 as the temperature increases from 150 to 300 K. The ρ_{nc}/ρ_n ratio for either set, just as the corresponding one for symmetric top CH_3Cl, does not approach unity even at 300 K. Taking $\rho_{0c}/\rho_n=1.25$ at 300 K we get, using the value for the polarizabilities given by Murphy,[3] $\rho_{0c}=0.94\times10^{-4}$. The measured value of the depolarization ratio by Murphy[3] at room temperature is 2.99×10^{-4}, close to the value $\rho_{0c}(4/1.25)=3.01\times10^{-4}$ one would get by ignoring the constraints imposed by the conservation of angular momentum.

CONCLUSION

The ratio of the calculated depolarization ratio to that given in literature, ρ_{nc}/ρ_n, for symmetric tops shows great variation with $|k|$ for a given value of j. However, for symmetric top CH_3Cl it shows little variation as a function of temperature, remaining about 0.72 over the 100–300 K temperature range. The ratio ρ_{nc}/ρ_n for asymmetric top water vapor also shows large variation with τ for a given value of j. However, it also shows little variation as a function of temperature and decreases from 1.32 (1.24) at 150 K to 1.27 (1.18) at 300 K. The ratio ρ_{nc}/ρ_n does not approach unity either for the symmetric top or the asymmetric top even at 300 K.

Bridge and Buckingham[2] have measured depolarization ratio $\rho_{0BB} \equiv 3\gamma^2/45\alpha_{av}^2 + 4\gamma^2$ of polarized light from a helium-neon gas laser by CH_3Cl at room temperature to be 7.66×10^{-3}. This expression can, with accuracy better than 0.5%, be approximated as $\rho_{0BB} \approx \gamma^2/15\alpha_{av}^2$. The ratio $(\gamma/\alpha)^2$ derived by these authors from the measured depolarization
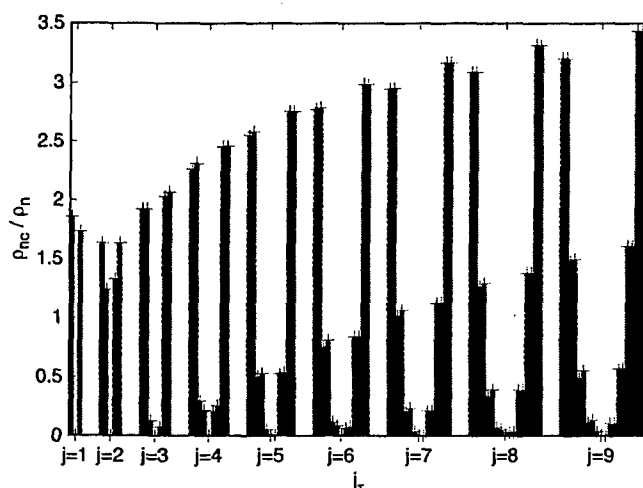

FIG. 4. The ratio of the calculated depolarization ratio to that given in literature, ρ_{nc}/ρ_n, for water vapor as a function of rotational level j_τ with τ increasing from right to left. The input polarizability data are from Murphy (Ref. 3). The other five sets gave similar figures and are therefore not shown.
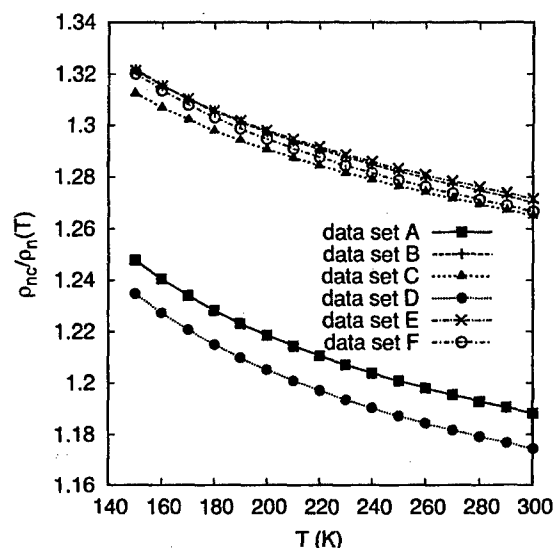
ratio is an overestimate by $4 \times 0.72 = 2.88$, the overestimate of the ratio of anisotropic to average (isotropic) polarizability (γ/α) being about 1.7.

By the same arguments the ratio of anisotropic to average (isotropic) polarizability of water vapor is overestimated[3] by about 2.2.

This underscores the fact that the contribution of the polarizability anisotropy to Rayleigh scattering by molecules is not correctly described in the literature.

ACKNOWLEDGMENTS

APPENDIX: NUCLEAR SPIN AND RAYLEIGH SCATTERING

The two nuclei of the hydrogen atoms in H_2O each have spin $1/2$, and are therefore fermions; the O atom has zero nuclear spin and is therefore a boson. The total nuclear spin of the two protons is zero (antisymmetric; degeneracy 1) or 1 (symmetric; degeneracy 3).

The ground state electronic and vibrational wave functions of H_2O are symmetric (do not change sign) upon interchanging the two H atoms. Therefore the product of the rotational wave function and nuclear spin wave function of H_2O has to be antisymmetric upon interchanging the two H atoms.

Para rotational wave functions ($++$ or $--$ symmetry) which do not change sign upon interchange of two H atoms must have an antisymmetric (total nuclear spin zero) nuclear wave function. These levels are unaffected by nuclear spin considerations.

Ortho rotational wave functions ($+-$ or $-+$ symmetry) which change sign upon interchange of two H atoms must have symmetric (total nuclear spin one) nuclear wave function. The combined rotational (j_τ) nuclear spin (S_N) wave function for the initial and final states can be written as

$$|JMj_\tau S_N\rangle = \sum_{m_1} C(j_\tau S_N J; M - m_1, m_1)|j_\tau, M - m_1\rangle|S_N, m_1\rangle,$$

$$(A1)$$

$$|J'M'j'_\tau S_N\rangle = \sum_{m_1} C(j'_\tau S_N J'; M' - m_1, m_1)|j'_\tau, M' - m_1\rangle$$

$$\times |S_N, m_1\rangle. \qquad (A2)$$

The function I_1 [Eq. (2)] for an asymmetric rotor becomes

$$I_1(j_\tau, \alpha) \equiv \left| \sum_{k_i, k_f, \kappa, m_1} C(j_\tau S_N J; M - m_1, m_1) C(j'_\tau S_N J'; M' \right.$$

$$- m_1, m_1) \chi_{\alpha,\kappa} a_{k_i} a^*_{k_f} \left[\frac{(2j_\tau + 1)}{(2j'_\tau + 1)} \right]^{1/2} C(j_\tau \alpha j'_\tau; k_i,$$

$$\left. - \kappa, k_f) \delta_{k_f, k_i - \kappa} C(j_\tau \alpha j'_\tau; M - m_1, M' - M) \right|^2.$$

$$(A3)$$

We now write, defining $q \equiv M' - M$,

$$C(j'_\tau S_N J'; M + q - m_1, m_1)$$

$$= (-1)^{j'_\tau - M - q + m_1} \left(\frac{2J + 1}{2S_N + 1} \right)^{1/2}$$

$$\times C(j'_\tau J' S_N; M + q - m_1, - M - q)$$

$$= (-1)^{j'_\tau - M - q + m_1 + j'_\tau + J' - S_N} \left(\frac{2J + 1}{2S_N + 1} \right)^{1/2}$$

$$\times C(J' j'_\tau S_N; - M - q, M + q - m_1), \qquad (A4)$$

$$C(j_\tau S_N J; M - m_1, m_1) = C(S_N j_\tau J; - m_1, m_1 - M), \qquad (A5)$$

$$C(j_\tau \alpha j'_\tau; M - m_1, q)$$

$$= (-1)^{j_\tau - M + m_1} \left[\frac{2j'_\tau + 1}{2\alpha + 1} \right]^{1/2}$$

$$\times C(j_\tau j'_\tau \alpha; M - m_1, m_1 - M - q)$$

$$= (-1)^{j_\tau - M + m_1} \left[\frac{2j'_\tau + 1}{2\alpha + 1} \right]^{1/2}$$

$$\times C(j'_\tau j_\tau \alpha; M + q - m_1, m_1 - M). \qquad (A6)$$

Using the relation

$$\sum_{m_1} C(J' j'_\tau S_N; - M - q, M + q - m_1) C(S_N j_\tau J; - m_1, m_1 - M)$$

$$\times C(j'_\tau j_\tau \alpha; M + q - m_1, m_1 - M)$$

$$= [(2\alpha + 1)(2S_N + 1)]^{1/2} W(J' j'_\tau J j_\tau; S_N \alpha)$$

$$\times C(J' \alpha J; - M - q, q)$$

$$= (-1)^{J' + M + q} [(2J + 1)(2S_N + 1)]^{1/2} W(J' j'_\tau J j_\tau; S_N \alpha)$$

$$\times C(J' J \alpha; - M - q, M), \qquad (A7)$$

we get

$$I_1(j_\tau, \alpha) \equiv \frac{(2j_\tau + 1)}{(2\alpha + 1)} (2J + 1) W^2(J' j'_\tau J j_\tau; S_N \alpha)$$

$$\times \left| \sum_{k_i, k_f, \kappa} \chi_{\alpha,\kappa} a_{k_i} a^*_{k_f} C(j_\tau \alpha j_\tau; k_i, - \kappa, k_f) \delta_{k_f, k_i - \kappa} \right|^2.$$

$$(A8)$$

This expression is very similar to the one for Rayleigh scattering from $O_2(^3\Sigma)$ molecule,

$$[I_1(N,J,N,J;S\alpha)]_{O_2} \equiv \frac{(2N+1)(2J+1)}{(2\alpha+1)}$$
$$\times C^2(N\alpha N;00)W^2(JNJN;S\alpha),$$

$$(A9)$$

where N and J are the initial and final rotational and total angular momenta, $S=1$ is the electron spin, and $\alpha=2$ is the rank of the polarizability tensor.

If we assume that the coupling of the nuclear spin with molecular rotation leading to splitting of the rotational levels is much smaller than either the linewidth of the rotational levels or the width of the laser line (~ 1 MHz) used to determine the depolarization ratio, we can then assume $j_\tau = j_\tau'$ and sum Eq. (8) over J. Using the relations

$$W^2(J'j_\tau'Jj_\tau;S_N\alpha) = W^2(j_\tau S_N\alpha J',Jj_\tau'),$$

$$(A10)$$

$$\sum_j (2J+1)(2j_\tau+1)W^2(j_\tau S_N\alpha J';Jj_\tau) = 1,$$

$$(A11)$$

we get

$$I_1(j_\tau,\alpha) \equiv \frac{1}{(2\alpha+1)}\left|\sum_{k_i,k_f,\kappa}\chi_{\alpha,\kappa}a_{k_i}a_{k_f}^*C(j_\tau\alpha j_\tau;k_i,\right.$$
$$\left. -\kappa,k_f)\delta_{k_f,k_i-\kappa}\right|^2.$$

$$(A12)$$

Finally recalling that for each value of j_τ there are $(2S_N+1)$

values of J' and summing over these values, we get

$$I_1(j_\tau,\alpha) \equiv \frac{(2S_N+1)}{(2\alpha+1)}\left|\sum_{k_i,k_f,\kappa}\chi_{\alpha,\kappa}a_{k_i}a_{k_f}^*C(j_\tau\alpha j_\tau;k_i,\right.$$
$$\left. -\kappa,k_f)\delta_{k_f,k_i-\kappa}\right|^2.$$

$$(A13)$$

[1] R. D. Sharma, J. Geophys. Res. (to be published).
[2] N. J. Bridge and A. D. Buckingham, Proc. R. Soc. London, Ser. A **295**, 334 (1966).
[3] W. F. Murphy, J. Chem. Phys. **67**, 5877 (1977).
[4] R. D. Sharma and L. A. Levin, J. Chem. Phys. **58**, 1660 (1973).
[5] R. N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, NY, 1987).
[6] D. M. Dennison and K. T. Hecht, *Molecular Spectra in Quantum Theory II. Aggregates of Particles*, edited by D. R. Bates (Academic, New York, 1962).
[7] G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945).
[8] H.-J. Werner and W. Meyer, Mol. Phys. **31**, 855 (1973).
[9] S. P. Liebmann and J. W. Moskowitz, J. Chem. Phys. **54**, 3622 (1971).
[10] J. F. Harrison, J. Chem. Phys. **49**, 3321 (1968).
[11] D. Rinaldi and J.-L. Rivail, Theor. Chim. Acta **32**, 243 (1974).
[12] R. Moccia, Theor. Chim. Acta **8**, 192 (1967).
[13] G. W. Kattawar, A. T. Young, and T. J. Humpherys, Astrophys. J. **159**, 1107 (1981).
[14] C. Asawaroengchai and G. M. Rosenblatt, J. Chem. Phys. **72**, 2664 (1977).
[15] G. D. Zeiss and W. J. Meath, Mol. Phys. **4**, 1155 (1977).